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REPORT

CD NO.

50X1-HUM

COUNTRY	USSR	DATE OF INFORMATION 1947
SUBJECT	Scientific - Chemistry	
HOW PUBLISHED	Monthly periodical	DATE DIST. 2 Jul 1950
WHERE PUBLISHED	Moscow	NO. OF PAGES 10
DATE PUBLISHED	Jan 1948	SUPPLEMENT TO . REPORT NO.
LANGUAGE	Russian	

THIS IS UNEVALUATED INFORMATION

PROBLEM OF THE CONNECTION BETWEEN VISCOSITY AND ELECTRICAL CONDUCTIVITY IN SOLUTIONS OF SALTS

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Submitted 12 Apr 1947

K. S. Yevstrop'yev [1, 2, 3], in treating the experimental data of a number of authors regarding the viscosity and electrical conductivity of aqueous solutions of salts, fused salts, and their binary mixtures, noted the presence of several relationships: (1) Johnston's equation, $\Lambda^n \eta$ equals const, where Λ is the molecular electrical conductivity and η is the viscosity [4], is correct for aqueous solutions of salts;   (2) the relation between lg $\varkappa$ or lg Λ (where $\varkappa$ is the specific electrical conductivity), and the composition of a binary mixture expressed in molecular percentages is represented in a majority of cases by a straight line, if the components form a simple eutectic; if the components form a chemical compound, this relation is represented by sections of straight lines intersecting at a point approximately coinciding with the composition of the compound; if the components form solid solutions, the dependence is represented by a smooth curve.

The present work deals mainly with solutions in organic substances, which Yevstrop'yev did not especially examine; he merely noted that the data on a solution of $AgNO_3$ in pyridine confirm the general picture.

Yevstrop'yev demonstrated the applicability of Johnston's equation to aqueous solutions of salts, finding a rectilinear dependence between lg Λ and lg η for a number of temperatures in solutions of NaCl, LiCl, $BaCl_2$, $ZnSO_4$, and others.

Treating the experimental data of Ye, Ya, Gorenbeyn [5, 6, 7] on nonaqueous solutions, we found that Johnston's equation is also applicable in this case, but at relatively high concentrations. As may be seen from Figures 1 - 4, which refer respectively to solutions of

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$SbBr_3$. $AlBr_3$ in benzene, toluene, and nitrobenzene, and to a solution of $CuBr$. Al_2Br_6 in Toluene, a deviation from rectilinear dependence is observed at various concentrations. For solutions of $SbBr_3$. $AlBr_3$ these concentrations are rather large, but for the second salt, apparently, they are below 3.7 percent (molecular percentage). On the diagrams, the concentration is designated beside each curve in molecular percentages, and the corresponding temperatures are indicated at the points on the curves.

It is possible to assume that the establishment of the lower limit of concentration at which Johnston's equation is observed for solutions may contribute to the understanding of their structure by establishing the connection between this limit and the other properties of the solutions. At present, nothing can be said concerning the existence of any such lower limits for aqueous solutions; Yevstrop'yev's calculations dealt with only one concentration of each salt with the exception of $NaCl$. for which is observed a parallelism of straight lines expressing the dependence of lg $\varkappa$ on lg η in 0.1 N and 4 N solutions $\underline{/} 1 \underline{/}$.

Solutions of $AlBr_3$ in ethyl bromide (Figure 5) give a picture similar to the preceding (Figures 1 - 4). It must be noted that in the given case, electrical conductivity develops as a result of the interaction of the salt and the solvent, because $AlBr_3$, unlike $SbBr_3$. $AlBr_3$, does not conduct in a fused condition. According to the data of Wohl and Wertyporoch $\underline{/} 8 \underline{/}$, based on the investigation of the migration of ions, the solvate $Al\underline{/} AlBr_4 \underline{/}_3$ is the electrolyte.

For solutions of $SbBr_3$. $AlBr_3$ in ethyl bromide (Figure 6) rectilinear dependence between lg Λ and lg η is absent at almost all concentrations. This circumstance may be explained by the insufficient stability of the solutions; for example, due to the decomposition of a binary salt under the influence of ethyl bromide.

We should further note that in nitrobenzene, the dielectric constant of which is rather large (ε equals 36.4), a normal dependence of conductivity on concentration is observed. In the other nonaqueous solutions in question, the dependence is anomalous. This may be seen if one compares the sequence of distribution of the curves in dependence on the concentration in nitrobenzene (Figure 3) and other solutions (Figures 1, 2, 4, 5, 6).

The presence of an exponential relationship between lg $\varkappa$ or lg Λ and lg η , on the one hand, and the composition of the binary mixture, on the other, was demonstrated by Yevstrop'yev in binary fusions of inorganic salts. If one regards a solution of salt in a liquid solvent, for example, in water or some organic substance, as a binary system, the following picture is revealed: the relation between lg η and the composition is expressed by two intersecting straight lines. This may be seen from the diagrams which were constructed by us on the basis of the respective conversion of the experimental data of Gorenbeyn $\underline{/} 5, 6 \underline{/}$ (Figures 7 - 11) and A. I. Rabinowitsch $\underline{/} 9 \underline{/}$ (Figure 12).

An exception occurs in the case of solutions of $CuBr$. Al_2Br_6 in toluene, where the dependence of lg η on the composition is completely rectilinear (Figure 14). The data for the calculation of the latter solutions were taken by us from Gorenbeyn $\underline{/} 7 \underline{/}$, who does not indicate whether or not saturation was reached. Therefore, nothing definite can be said about the possibility of a break on the curve representing the dependence of lg η on the composition with further increase of concentration. The figures standing by the indices of η and also by the indices of Λ on the diagrams beside the corresponding curves designate the temperature. The content of salt in the solution (molecular percentage) is indicated in all cases on the axis of the abscissas.

Let us examine the diagrams in Figures 7 - 12 and 14. The intersection of straight lines, turned at an angle from the axis of the composition (Figures 10, 12), was not observed in Yevstrop'yev's work. Such an intersection may be interpreted within the framework of the established conceptions of physicochemical analysis as an indication of the presence of a chemical compound. The position of the point of intersection, which we will call the angle point, corresponds to the ratio 1:8 for solutions of $AgNO_3$ in water (Figure 12); but it does not correspond to any definite stoichiometric ratio for solutions of $SbBr_3$. $AlBr_3$ in ethyl bromide (Figure 10).

The intersection turned at an angle to the axis of the composition corresponds to the ration 1:8 for solutions of $SbBr_3$. $AlBr_3$ in toluene (Figure 8); and 1:3 for $AlBr_3$ in ethyl bromide (Figure 11). It does not seem possible, however, without an appropriate investigation to interpret this circumstance as an indication of the presence of definite chemical compounds by means of a transference to the given solutions of the conclusions made by Yevstrop'yev for binary fusions of salts.

It must be noted that the abscissa of the angle point does not depend on the temperature (Figures 7 - 10). In the case of solutions of $AlBr_3$ in ethyl bromide (Figure 11) a slight displacement is noted; this displacement is possibly caused by a chemical interaction between the dissolved substance and the solvent. In Yevstrop'yev's work $/ 3 /$ there is a similar displacement on the diagram of lg $\varkappa$ and the composition for the system of $CdCl_2$ - $TlCl$. Yevstrop'yev, however, does not interpret this displacement in the sense given by us; for according to his judgment the presence in general of an angle point in the fusions studied by him indicates the formation of a chemical compound.

If one turns to the consideration in our objectives of the connection between the logarithm of conductivity and composition, in general a more complicated picture is observed than in the cases of the connection of the logarithm of viscosity and composition. The concurrence of the abscissas of the angle points at curves lg Λ and lg η is observed in the case of solutions of $AgNO_3$ in water (Figure 12) and solutions of $SbBr_3$. $AlBr_3$ in nitrobenzene (Figure 9). Also, the angles are turned to the opposite sides in accordance with the fact that an increase of electrical conductivity corresponds to a drop in viscosity. This observation is not correct for specific electrical conductivity (Figure 12), the values of which give an obscure picture in other cases as well.

The indicated concurrence of the abscissas of the angle points, however, is not compulsory for all aqueous solutions. This may be seen from Figure 13, which refers to aqueous solutions of $AgTl(NO_3)_2$, for which complicated relationships may be seen. Apparently, this binary salt undergoes decomposition into its component salts to a certain extent. The diagram is constructed on the basis of the conversion of the data of A. I. Rabinowitsch $/ 9 /$.

In solvents with low dielectric constants benzene, toluene, ethyl bromide), a direct comparison of the relations between lg Λ and the composition and lg η and the composition is not feasible (Figures 7, 8, 10, 11, 14). In certain cases there is a sharp drop in conductivity corresponding to the angle point on curve lg η (Figures 7, 8). It is interesting that for these same cases, the concentration corresponding to the angle point on curve lg η coincides approximately with the lower limit of concentrations at which Johnston's equation is observed (Figures 1, 2). The picture is complicated in the case of solutions of $SbBr_3$. $AlBr_3$ in ethyl bromide, where no noticeable points on the curve of viscosity correspond to the maximum on the curve of conductivity (Figure 10); and in the case of solutions of $CuBr$. Al_2Br_6 in toluene (Figure 14), where the relation between lg η and the composition is completely rectilinear, but the course of the dependence of lg Λ on the composition has a complicated character.

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It should be noted, additionally, that we have avoided encumbering the reproduced diagrams with all the isotherms characterizing the dependence of $\lg \Lambda$ on the composition, for in every nonaqueous solution examined by us they have a very similar character.

The material expounded above makes it possible to conclude that the dependence of $\lg \eta$ on the composition frequently finds no parallel with the dependence of $\lg \Lambda$ on the composition. This circumstance has an essential importance for the consideration of the problem of the applicability of a simple correction for viscosity in the case of electrical conductivity. As is known, this correction has the following form:

$$\Lambda' = \Lambda \cdot \frac{\eta}{\eta \infty} ,$$

where η is the viscosity of the solution in poises; $\eta \infty$ is the viscosity of the solvent; and Λ is the measured molecular electrical conductivity. The correction assumes an inverse ratio between viscosity and electrical conductivity. The problem of the presence of an inverse ratio may be solved by plotting the dependence of $\lg \Lambda \eta$ on the composition. This may also be accomplished graphically by the addition of the ordinates $\lg \eta$ and $\lg \Lambda$ for each composition.

It is fully evident that with the presence of an inverse ratio the curve $\lg \Lambda \eta$ must be parallel to the axis of composition. This parallelism in the systems studied by us takes place only in solutions of $AlBr_3$. $SbBr_3$ in nitrobenzene in concentrations from 0.6 ($\mathcal{P}$ equals 17,200) to 8-10 molecular percent ($\mathcal{P}$ equals 1,200 milliliters) (Figure 9); and in solutions of $AgNO_3$ in water in concentrations from 3.8 (26.5 percent by weight) to 15.5 molecular percent (63.1 percent by weight). In the case of the other solutions, there can be no question of parallelism, because of the obvious disparity between the course of the curves of $\lg \Lambda$ and the composition and $\lg \eta$ and the composition (Figures 7, 8, 10, 11, 14). The same must be said of the curves of $\lg \varkappa$ and the composition (Figures 8, 10, 14). In the case of the absence of parallelism of a rectilinear section of the curve $\lg \Lambda \eta$ to the axis of the composition, this section has an ascending character towards higher concentrations (Figures 9, 12, 13).

The parallelism of the values of $\lg \Lambda \eta$ to the axis of the composition in a definite interval of concentrations is evidence of the fact that here: (1) the composition of the electrolyte remains unchanged; (2) the structure of the solution does not undergo changes; (3) the degree of dissociation of the electrolyte does not depend on the dilution.

There is a rather extensive literature on the problem of a simple correction for viscosity in the Values for electrical conductivity (see Gatchek $\boxed{11}$). From this, one may obtain the general indication that this correction is definitely applicable in the zone of concentrations in which the viscosity of the solution does not greatly deviate from the viscosity of the pure solvent. In the solutions analyzed by us, one may see that a rigid inverse ratio between viscosity and molecular electrical conductivity is also observed in individual cases in concentrated solutions greatly differing from the pure solvent in viscosity.

Ye. Ya. Gorenbeyn $\boxed{5}, 6, 7, \boxed{12}$ applies a simple correction for viscosity electrical conductivity in the case of all solutions analyzed in the present work. As could be seen from what has been said, the application of such a correction is, in almost all cases, unfounded. The correlations between viscosity and electrical conductivity have proved to be complicated and diverse. Therefore, the generalizing conclusions made by Gorenbeyn, on the basis of a uniform and unconditional application of the correction, do not correspond to fact $\boxed{10}$.

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Conclusions

The relation between viscosity, electrical conductivity, and composition for the following solutions has been considered: for aqueous solutions of $AgNO_3$ and $AgTl (NO_3)_2$ investigated by A. I. Rabinowitsch; for solutions of $AlBr_3$. $SbBr_3$ in ethyl bromide; benzene, toluene, and nitrobenzene; and for solutions of $CuBrAl_2Br_6$ in toluene and of $AlBr_3$ in ethyl bromide, investigated by Ye. Ya. Gorenbeyn.

The following results were obtained:

1. The dependence of viscosity on molecular electrical conductivity follows Johnston's equation $\Lambda^n\eta$ equals const above a definite concentration in the case of all the nonaqueous solutions mentioned except for solutions of $SbBr_3$. $AlBr_3$ in ethyl bromide.

2. The relationship of viscosity composition in a majority of cases does not correspond to the relationship of molecular electrical conductivity-composition An inverse ratio between molecular electrical conductivity and viscosity is observed in solutions of $AgNO_3$, in water at 100 degrees centigrade at concentrations from 3.8 to 15.5 molecular percent; and in solutions of $SbBr_3$. $AlBr_3$ in nitrobenzene at concentrations from 0.6 to 8 - 10 molecular percent.

3. The application of a simple correction for viscosity to values for electrical conductivity, according to the expression $\Lambda' = \Lambda \cdot \dfrac{\eta}{\eta \infty}$

(where Λ is the measured molecular electrical conductivity; η is the viscosity of the solution; and η_∞ is the viscosity of the solvent) is inadmissible without a special study of the experimental data.

4. There is no basis for the universal application of the indicated correction to all of the solutions considered, as was done by Gorenbeyn.

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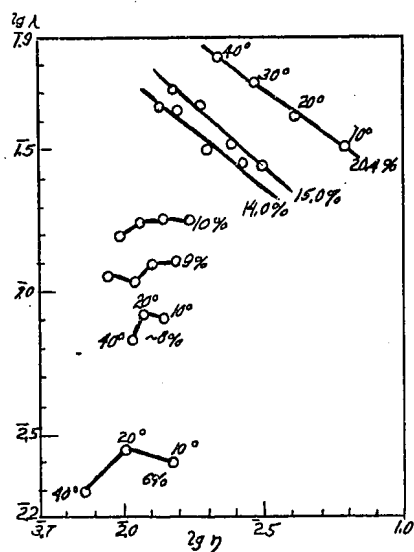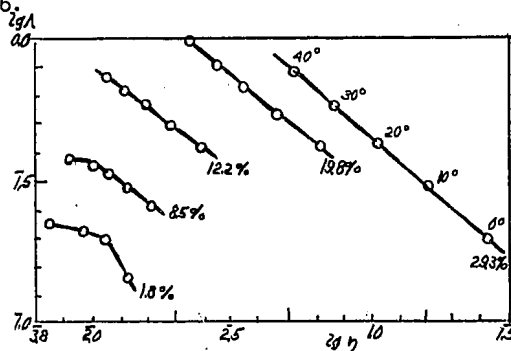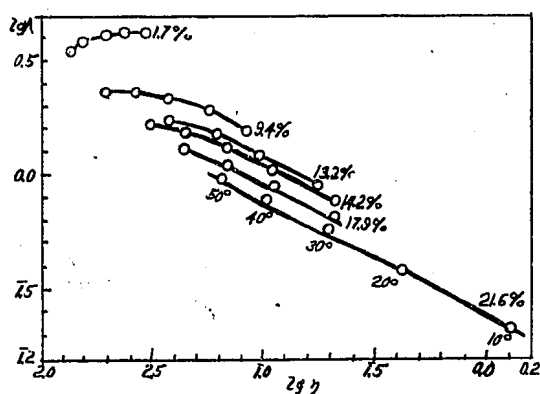
[Appended figures follow:]

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Figure 1. System $SbBr_3 \cdot AlBr_3 - C_6H_6$.

Figure 2. System $SbBr_3 \cdot AlBr_3 - C_6H_5CH_3$

Figure 3. System $SbBr_3 \cdot AlBr_3 - C_6H_5NO_2$.

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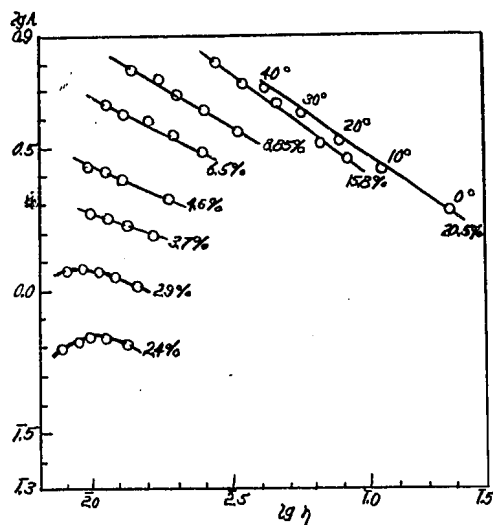
Figure 4. System $CuBr \cdot Al_2Br_6 - C_6H_5CH_3$.
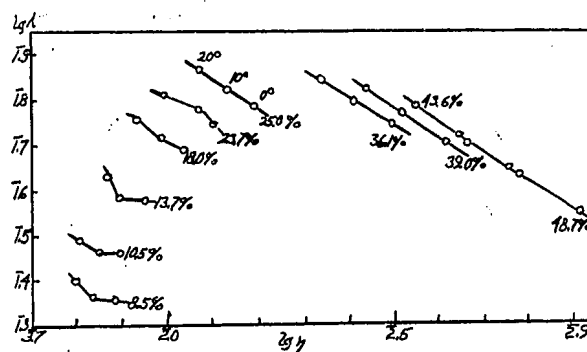
Figure 5. System $AlBr_3 - C_2H_5Br$.
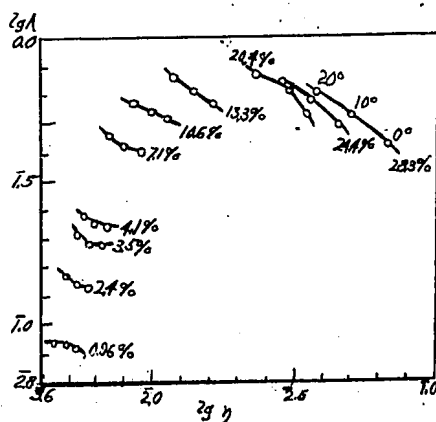
Figure 6. System $SbBr_3 \cdot AlBr_3 - C_2H_5Br$.

Figure 8. System $SbBr_3 \cdot AlBr_3 - C_6H_5CH_3$.
/Note: The numbers on the axis of the ordinates in this diagram should be raised two divisions; that is, the division designated 2, 5 on the diagram actually corresponds to 2, 3 and so forth./
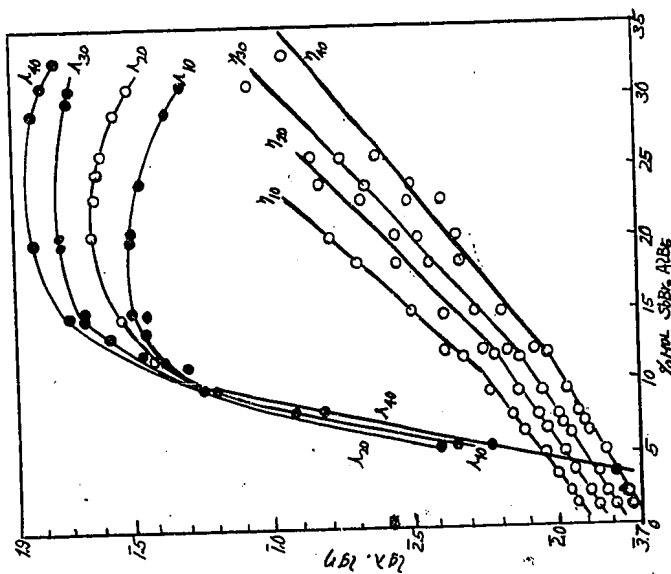
Figure 7. System $SbBr_3 \cdot AlBr_3 - C_6H_6$.
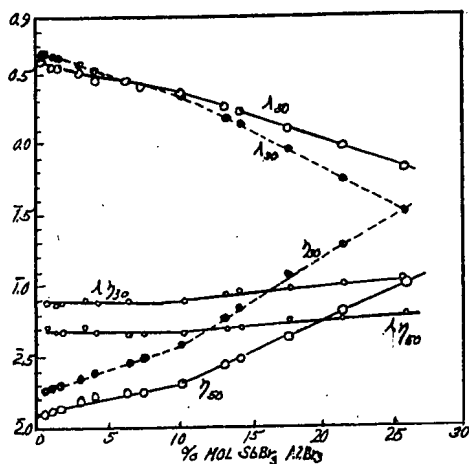
Figure 9.   System $SbBr_3 \cdot AlBr_3 - C_6H_5NO_2$.
On the axis of the ordinates there is a
single scale for $\lg \eta$, $\lg \Lambda$, $\lg \eta \Lambda$
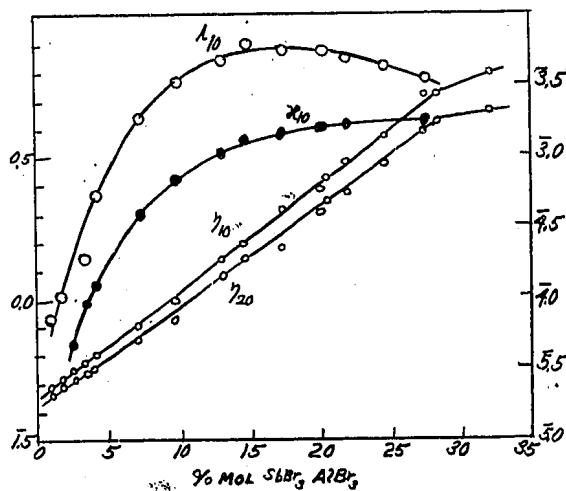
Figure 10.   System $SbBr_3 \cdot AlBr_3 -$
C_2H_5Br. The left scale is $\lg \eta$,
$\lg \Lambda$; the right scale is $\lg \varkappa$.
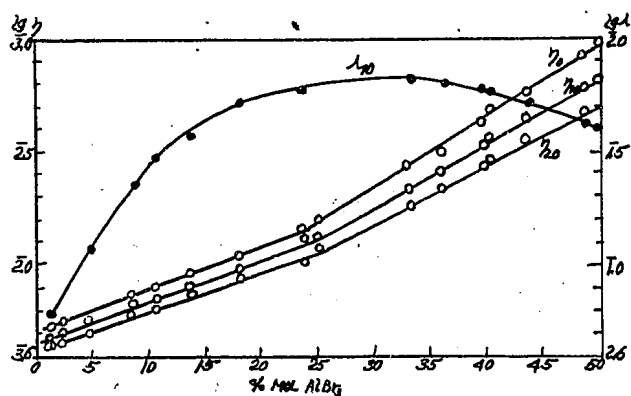
Figure 11. System $AlBr_3 - C_2H_5Br$.

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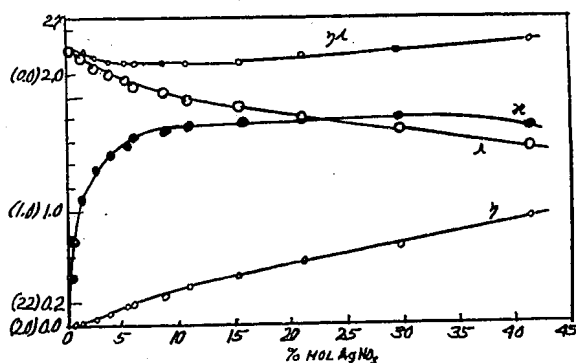
Figure 12. System of $AgNO_3$ - H_2O at 100°. On the axis of the ordinates there is a single scale for $\lg \eta$, $\lg \lambda$, $\lg \eta \lambda$. The figures in parentheses are the values of $\lg \varkappa$.
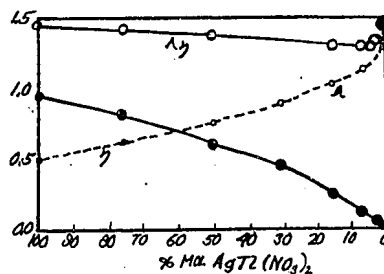

Figure 13. System $AgTl(NO_3)_2$ - H_2O at 100°. On the axis of the ordinates there is a single scale for $\lg \eta$, $\lg \lambda$, $\lg \lambda \eta$.
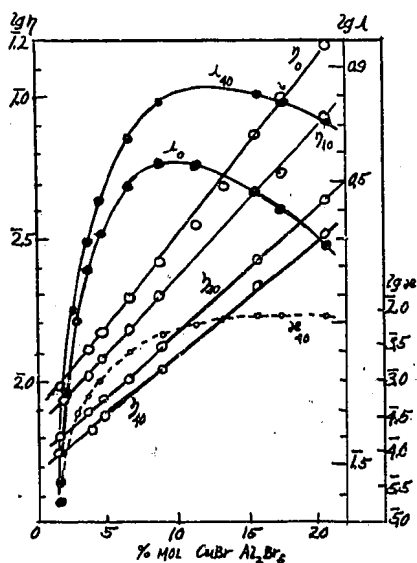

Figure 14. System $CuBr \cdot Al_2Br_6$ - $C_6H_5CH_3$.

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